



PATENT SPECIFICATION

DRAWINGS ATTACHED

972,140

Date of Application and filing Complete Specification: Dec. 21, 1961.

No. 45908/61.

Application made in United States of America (No. 78162) on Dec. 23, 1960.

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COMPLETE SPECIFICATION

Removal of Acidic Gases from Gaseous Mixtures

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ERRATA

SPECIFICATION No. 972,140

10

Page 2, line 29, delete "content"

Page 4, line 3, for "components" read "component"

Page 6, line 96, for "cas" read "gas"

Page 7, line 52, for "slphur" read "sulphur"

15

Page 9, line 47, after "achieve" insert "a"

Page 9, line 121, for "galosine" read "gasoline"

THE PATENT OFFICE

7th April 1965

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subsequently decomposed, usually by heating, to regenerate the solution utilized as an absorber and to drive off the gas absorbed.

25 In many cases aqueous solutions of alkanolamines are utilized. Such solutions, however, have only a relatively limited solubility for acid gases even when the latter are under a high partial pressure. This results in the necessity to recycle and treat unduly large quantities of such solutions unless only a fractional removal of the acid gas from its admixture with hydrocarbons or other gaseous materials is accepted. Another disadvantage of the application of these solutions is that quite often rather serious corrosion of the processing equipment is encountered.

40 As distinct from these so-called "chemical solvents," certain classes of materials are regarded as "physical solvents." These include such materials as glycols which appear to act in a purely physical manner, absorbing acidic gases physically without the formation of any apparent reaction product. Mixtures

efficient and complete removal of the acidic contaminants. None of the known absorbents is satisfactory in this respect.

70 A number of problems have arisen in addition to those outlined above. The thermal stability of organic solvents becomes a problem especially during the stripping step wherein the fat solvent is heated to a temperature sufficiently high to separate the acid gases from the solvent. It is often found that solvents show an undue lack of thermal stability under these conditions. The resulting decomposition of the solvent constitutes a major cost factor in the operation of the process. Another major problem is caused by the temperature difference between the absorption column and the stripping column. While heat losses can be minimized to a large extent by heat exchanging the various streams involved in the process, it is still often necessary to utilize external cooling means to cool the recycle stream of clean regenerated solvent to the absorber, as well as to employ heating means for heating the

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COMPLETE SPECIFICATION

Removal of Acidic Gases from Gaseous Mixtures

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of the Netherlands, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the separation of acidic gases from gaseous mixtures by means of a selective absorbent. The invention is applicable more particularly, but not exclusively, to the case where the acidic gases contain sulphur.

A number of methods have previously been proposed for the purification of mixtures of hydrocarbon gases contaminated with such materials as hydrogen sulphide, carbonyl sulphide and carbon dioxide. Some of these methods involve the formation of alkanolamine salts of the acid gases, the salts being subsequently decomposed, usually by heating, to regenerate the solution utilized as an absorbent and to drive off the gas absorbed.

In many cases aqueous solutions of alkanolamines are utilized. Such solutions, however, have only a relatively limited solubility for acid gases even when the latter are under a high partial pressure. This results in the necessity to recycle and treat unduly large quantities of such solutions unless only a fractional removal of the acid gas from its admixture with hydrocarbons or other gaseous materials is accepted. Another disadvantage of the application of these solutions is that quite often rather serious corrosion of the processing equipment is encountered.

As distinct from these so-called "chemical solvents," certain classes of materials are regarded as "physical solvents." These include such materials as glycols which appear to act in a purely physical manner, absorbing acidic gases physically without the formation of any apparent reaction product. Mixtures

of glycols with amines are known, particularly for the treatment of liquid hydrocarbon products for the removal of mercaptans, hydrogen sulphide and other acidic substances. However, glycols have not been found to be very attractive in view of the limited solubility of acidic gases therein. Aqueous dispersions of glycols are no better in this respect and, moreover, may exhibit extreme corrosiveness toward processing equipment.

Another disadvantage of the use of aqueous solution is the necessity for a separate dehydration step, since such absorbents do not remove water from the gases. Since in almost all instances water cannot be tolerated in the sweet gas stream, its removal constitutes an additional cost factor in the processing of gases.

One of the problems encountered, especially in the processing of gases having high partial pressures of acidic components, is the efficient and complete removal of the acidic contaminants. None of the known absorbents is satisfactory in this respect.

A number of problems have arisen in addition to those outlined above. The thermal stability of organic solvents becomes a problem especially during the stripping step wherein the fat solvent is heated to a temperature sufficiently high to separate the acid gases from the solvent. It is often found that solvents show an undue lack of thermal stability under these conditions. The resulting decomposition of the solvent constitutes a major cost factor in the operation of the process. Another major problem is caused by the temperature difference between the absorption column and the stripping column. While heat losses can be minimized to a large extent by heat exchanging the various streams involved in the process, it is still often necessary to utilize external cooling means to cool the recycle stream of clean regenerated solvent to the absorber, as well as to employ heating means for heating the

fat solvent passing from the bottom of the absorber column to the stripping column. Still another major cost factor is the stripping steam requirement, which is very high for many solvents.

The present invention enables disadvantages inherent in the use of previously known absorbents to be overcome.

According to the invention, a process for the removal of acidic gases from a gaseous mixture comprises contacting the gaseous mixture with a liquid absorbent comprising a basic component consisting of at least one amine having a weakly basic character in the range of pK_b at 25°C of 3 — 14, and a selective solvent comprising at least one component selected from aliphatic acid amides, cyclotetramethylene sulphone and its derivatives and perhaloalkanes, and separating the resulting essentially acid-free gas from the liquid absorbent containing the absorbed acidic gases.

The absorbent containing the acidic gases may be regenerated.

In some cases it has been found advantageous to use in this process an absorbent which contains a small amount of water, in the range of 1-15% wt. The amine content of the absorbent is usually within the range of 7.5 and 70% wt., preferably of 15-35% wt. An absorbent containing 20-30% wt. amine has been found very suitable. The balance of the absorbent consists essentially of a physical solvent and, optionally, water in a percentage as indicated above.

As indicated, the chemical solvent part of the absorbent comprises a weakly basic amine, or a mixture of such amines. The basic strength of a compound is conveniently expressed in terms of the negative logarithm of the basic dissociation constant pK_b . Thus a strong base has a low pK_b , while a weak base has a value approaching the upper limit $pK_b=14$. Bases suitable for the process according to the invention have a pK_b at 25°C in the range of 3 to 14. Alkanolamines are suitable, especially those having 1 to 4 and preferably 2 to 3 carbon atoms per alkanol radical while especially such dialkanolamines can be used with advantage. Typical species are, inter alia, monoethanolamine, diethanolamine, diisopropanolamine and mixtures thereof. Other amines which can be put to use are alkylamines, phenyl alkylamines, alkoxy alkyl and alkoxy aryl amines. Typical species of these sub classes are dimethylamine, methyl ethyl amine, phenyl ethyl amine, 2,4-phenylene diamine and methoxy ethyl diamine.

As indicated, the physical solvent part of the absorbent comprises one or a mixture of components selected from cyclotetramethylene sulphones, aliphatic acid amides and perhalo alkanes.

The derivatives from the basic sulphone

cyclotetramethylene sulphone or thiophene tetrahydro-1, 1-dioxide, which is also known as sulfolane, should preferably have not more than 4, more preferably not more than 2 alkyl substituents in the tetramethylene sulphone ring.

Sulfolane is the preferred species of this class of compounds.

Amides specifically suitable are the dialkyl-N-substituted aliphatic acid amides, a preferred species being dimethyl formamide. Preferably the alkyl groups directly attached to the nitrogen atom have from 1 to 4 carbon atoms each while an acid with 1 to 4 carbon atoms per mol. is preferred as well.

Apart from dimethyl formamide mentioned above other species in this preferred sub-class include methyl ethyl formamide, diethyl formamide, propyl methyl formamide, dibutyl formamide, dimethyl acetamide, methyl ethyl acetamide, formamide and acetamide.

Suitable perhaloalkanes include perfluoro alkanes such as perfluoro ethane and perfluoro butane as well as perchloro alkanes such as perchloro propane.

Gaseous mixtures which can advantageously be treated by the process according to the invention include natural gas, refinery gas or flue gas. The process is particularly attractive for the treatment of gases containing a very high proportion of acid gases such as hydrogen sulphide and carbon dioxide. The process may be adapted to treat such feedstocks which also contain higher molecular weight hydrocarbons, suitable as gasoline components (herein termed "gasoline-type hydrocarbons"), in which case such a feedstock can be split up into acid gases, dry sweet gas and gasoline-type hydrocarbons. It is also possible to separate the latter hydrocarbons into aromatic and non-aromatic hydrocarbons.

The invention may be performed in various ways, and some specific processes will now be described by way of example with reference to the accompanying drawings, in which:

Figure I shows one form of apparatus suitable for carrying out the process of the invention;

Figure II shows an apparatus suitable for carrying out the process of the invention where the absorbent contains 1 to 15% water;

Figure III shows apparatus suitable for carrying out a preferred process involving maximum utility of the absorption streams and separation of aromatics from non-aromatic hydrocarbons of higher than the normally gaseous range;

Figure IV shows relative solubilities of hydrogen sulphide in liquid absorbents of this invention compared with prior art absorbents; and

Figure V shows a similar graph of the

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relative solubilities of carbon dioxide in absorbents of this invention and in prior art absorbents.

In Figure IV the volume of hydrogen sulphide absorbed pervolume solvent (vertical axis) is plotted as a function of the hydrogen sulphide partial pressure in kg/cm² (horizontal axis), while in Figure V the same co-ordinates are given for the carbon dioxide absorption. This relation is indicated in both graphs for 100% dimethyl formamide (line A), for 20% aqueous diethanolamine (line B) and for a mixed absorbent consisting of 20% diethanolamine and 80% dimethyl formamide (line C), while in Figure V line D indicates this relation for a mixed absorbent consisting of 10% diethanolamine and 90% dimethyl formamide.

The principal advantage of the process of this invention is the high degree of removal at very low solvent flows of acidic gas components from gaseous mixtures containing progressively smaller amounts of acidic gas. For example, when a gaseous mixture enters the lower part of an absorber column in countercurrent to a descending stream of liquid absorbent efficient operation is obtained by use of an absorption composition of the present invention, since a high degree of absorption is obtained under the relatively high initial partial pressure of acidic gases and this high rate of absorption is maintained even as the partial pressure of acidic gas progressively decreases as the gas mixture proceeds upward in the column.

The advantage of using a mixed absorbent according to this invention as compared with the use of an amide as the sole extraction

solvent or with the use of aqueous alkanolamine solutions is further indicated by the following comparative data (see Table, and Figures IV and V). In the Table below it will be seen that at high partial pressures of hydrogen sulphide the solubility of hydrogen sulphide is extremely high in dimethyl formamide as a sole solvent but that it is essentially the same in a mixture of 20% diethanolamine—80% dimethyl formamide solution, while in a 20% aqueous diethanolamine solution the absorption of hydrogen sulphide is extremely low in comparison. However, at the lowest partial pressure of hydrogen sulphide tested (0.007 kg/cm² abs.), the solubility of hydrogen sulphide in pure dimethyl formamide is extremely low. This indicates that when an acid gas is stripped by counter-current contacting with an absorption solvent the effluent gas will probably contain appreciable amounts of residual hydrogen sulphide. The data indicate that the use of aqueous diethanolamine at these low partial pressures of hydrogen sulphide would result in a high solubility of the latter. However, as stated above, the aqueous solution are totally inadequate at higher pressures which would be encountered initially in stripping a very sour gas stream. Consequently, the intermediate and substantial solubility of hydrogen sulphide in the diethanolamine-dimethyl formamide mixture of the invention solves the problem, namely high initial solubility at high partial pressures of hydrogen sulphide and satisfactory sufficient solubilities of the latter at low partial pressures of hydrogen sulphide.

TABLE

Partial pressure of H ₂ S in feed, kg/cm ² abs.	Solubility of H ₂ S(STP) in ml/ml solvent		
	Dimethyl 20% Formamide 80%	Diethanolamine Dimethyl formamide	20% Diethanolamine 80% water
21.1	3860	3900	84
7.0	238	250	58
0.7	25.5	50.6	42
0.07	2.2	11.2	20
0.007	0.2	2.8	7.6

Quantitative data illustrating the advantage of mixed solvents comprising sulpholane as the "physical solvent" components are given in the following Table.

TABLE

SOLUBILITY OF H_2S (STP) IN ML/ML SOLVENT AT 40°C

Partial pressure of H_2S kg/cm ² abs.	Diethanol amine-sulpholane (a)	Diethanol amine-aqueous sulpholane (b)	Diethanol amine- H_2O (c)	Sulpholane
7.1	150	150	45	88
0.7	50	56	36	8
0.07	10	13	17	0.7
0.007	2	2.9	5.5	0.07
0.0007	0.4	0.7	1.7	0.007

(a) 30% wt. DEA, 70% wt. Sulpholane.

(b) 30% wt. DEA, 6% wt. H_2O , 64% wt. Sulpholane.

(c) 22% wt. DEA, 78% wt. H_2O .

5 An engineering estimate of each of the systems considered in the above Table showed that the capital cost of the mixed absorbent process of the invention is roughly only about one half of the cost of each of the other two systems.

10 The advantages of the version of the process where a mixed absorbent is used containing a restricted percentage of water are mainly apparent in the stripping of the fat absorbent. It has been found that in stripping a fat mixed absorbent of the invention to remove hydrogen sulphide, the steam requirement per unit volume of mixed absorbent is much lower than for other solvent systems.

15 For instance, stripping steam requirements with a typical "chemical solvent" (such as aqueous diethanolamine) is three times higher than that of the present mixed absorbent. Furthermore, in most applications, the

25 volumetric requirements for hydrogen sulphide absorption are much lower in the case of aqueous mixed absorbent than when using the conventional aqueous alkanolamines. Hence, the process heat load, an item accounting for over 50% of the process operating cost, is about one quarter or less than that of processes using aqueous alkanolamines.

30 If the acid gases contain higher molecular weight hydrocarbons (applicable as gasoline components) such as is often the case in natural gas, the acid gases may be passed through a sponge oil comprising gas oil hydrocarbons (C_{12-18} hydrocarbons) wherein the gasoline components are absorbed for subsequent recovery, while the acid gases freed from these components are obtained in a greater purity.

40 Analyses of two gases which may be treated with the process according to the invention

are given below:

TABLE

Component	1	2
	Volume %	Volume %
Hydrogen sulphide	31.48	7.5
Carbon dioxide	7.10	1.3
Nitrogen	4.52	23.0
Methane	50.35	43.0
Ethane	2.16	3.3
Propane	0.74	0.8
Isobutane	0.23	0.3
Normal butane	0.41	0.2
Isopentane	0.31	—
Normal pentane	0.39	—
Hexanes	0.53	—
Heptanes and higher	1.78	—
Hydrogen	—	20.1
Pentanes and higher	—	0.5

5 The process of the invention may be utilized for the purification of highly acid gases such as that exemplified in column 1; it may also be employed for the treatment of gases wherein the acid gas content is relatively low such as a refinery gas having a composition such as that given in column 2.

10 The basic step in the process of the invention comprises intimate contacting between the gaseous mixture and the liquid absorbent mixture, usually at pressures in the range 7 to 70 kg/cm². Countercurrent contacting is preferred in the absorber column (although this engineering detail may be varied according to a specific plant design). A highly preferred aspect of the operating of the absorber column is to conduct the absorption under rectified absorber conditions at temperatures in the range of about 25°C to about 135°C (preferably 30-80°C), the temperature of the bottom of the absorber column being about 10°C to 85°C higher than the temperature in the top part of the absorption zone. Normally, intimate contact-
25 ing is effected in a vertical column, the sweet

dry gas leaving the column near or at the top while the fat absorbent solution (containing extracted acidic gases) leaves at or near the bottom of the column. Heat may be supplied if necessary by means of a steam coil or reboiler near the bottom of the column. The column is preferably supplied with fractionating plates, baffles or other contacting means.

30 The fat absorbent solution contains dissolved acid gases such as hydrogen sulphide and carbon dioxide, together with possible contaminating proportions of hydrocarbons, originally present in the gaseous mixture. Under the preferred rectified absorption conditions, the proportion of hydrocarbons contaminant to hydrogen sulphide is maintained at a minimum level, the maximum ratio of hydrocarbon to hydrogen sulphide or other acid gas being about 2 to 100 parts by weight. In the absence of rectification, the proportion of hydrocarbon contaminants which may occur in the fat absorbent solution is much greater, and in some cases it may well exceed the amount of hydrogen
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sulphide present. This is of particular disadvantage when the hydrogen sulphide is to be utilized subsequently for the preparation of elemental sulphur or for other known purposes.

5 The fat absorbent solution may be conducted from the bottom portion of the absorber column under high pressure, preferably to a flashing zone wherein the pressure is
10 reduced to 1.15 to 8 kg/cm²abs. for the purpose of removing a major portion of the acid gas and substantially all of the co-absorbed hydrocarbons. In the same or a
15 subsequent column, referred to as a gas stripper, the remaining solution is reduced somewhat in pressure and heated to a temperature sufficient to volatilize the remaining acid gases and water therefrom, both of which leave the stripping column at various ports near
20 the top. Alternatively, the fat absorbent may be sent directly from the absorber column to the gas stripper.

One of the chief advantages of the use of the aqueous mixed absorbent in a preferred embodiment of the present invention is experienced during the stripping operation. The presence of the highly restricted proportion of water (1-15%) has been found to permit the use of substantially lower
25 stripping temperatures than are required when a water-free absorbent is used. Thus, it is possible to employ stripping temperatures between about 112°C and about 190°C at pressures between about 1 and about 3.5
30 kg/cm²abs. when the restricted proportion of water is present, while for the complete stripping of corresponding anhydrous absorbents temperatures are required which may be over 100°C higher. The use of these lower
40 temperatures has several advantages. Firstly, the thermal degradation of the organic solvent fractions of the mixed absorbent is greatly reduced. Secondly, the differential in temperature between the absorber column and the stripping column is held to a minimum, thus making the heating and cooling requirements far less stringent than in an anhydrous absorbent system.

50 The proportion of water is held within the restricted range of 1-15% for the reason that if greater proportions of water are employed, the feed gas from which acid gases are being extracted is not sufficiently dehydrated to meet the specification normally made for gas to be transported by pipeline to consuming areas. A way to reduce the water content of the sweet gas further will be discussed hereinafter.

60 In accordance with one feature of the present invention gasoline-type hydrocarbons still admixed with the acid gases may be removed therefrom by contacting the acid gases with a sponge oil comprising gas oil hydrocarbons. The latter normally have from
65 12 to 18 carbon atoms per molecule. In this

way the gasoline-type hydrocarbons are extracted from the acid gases. The acid gases are then ready for storage or further use, for instance the production of sulphur, for instance in a Claus plant.

70 The removal of gasoline-type hydrocarbons from the acid gases with a sponge oil may be effected in a top section of the flasher or stripping column or in separate scrubber towers following either the flasher or stripper, preferably at a temperature of 27-85°C.

75 The fat sponge oil, containing extracted gasoline-type hydrocarbons is warmed, for instance by indirect heat exchange with lean sponge oil being recycled to the sponge oil scrubbing tower. In the sponge oil stripping section the fat sponge oil may be heated still further, for instance by means of a steam coil at the bottom of the stripper, to a temperature in the order of 150-205°C, for the purpose of evaporating the gasoline-type hydrocarbons. The pressure is such that at this bottom tower temperature the gasoline-type hydrocarbons are readily volatilized, pressures of about 2 kg/cm²abs. or less being preferred. The volatilized gasoline-type hydrocarbons may be utilized as such or may be further purified if necessary in a gasoline-type hydrocarbon purifier tower wherein they are free from any residual acid gas by rectification.

Three specific examples of the process according to the invention will now be given.

EXAMPLE I (see Figure I).

100 A refinery gas containing 8% hydrogen sulphide, 2% carbon dioxide, the remainder being light hydrocarbons and inert gases was treated according to the process of the invention. The feed from a source 1 is injected
105 into the lower section of a rectified absorber column 2, fitted with a reboiler (not shown) and fractionation plates (not shown) under a pressure of about 17.5 kg/cm²abs. and a temperature of about 32°C. The bottom of the absorber column is maintained at a temperature of about 65°C by means of a reboiler (not shown), while the top section of the absorber column has a temperature of about 38°C. The lean mixed solvent absorbent, comprising 20% by weight diethanolamine and 80% by weight of dimethyl formamide enters the absorber column 2 by means of line 3 at a temperature of about 32°C. Hydrogen sulphide, any water and a small amount of hydrocarbons are absorbed by the absorbent from the sour feed. Dry sweet hydrocarbon gas leaves the absorption section of the absorber column via a line 11.

115 The fat absorbent containing absorbed acid gases leaves the bottom of the absorber column 2 by means of a line 12 and passes under substantially reduced pressure to a stripper column 13 which is heated by means

of reboiler 14. The acid gases being removed by heating in the stripper column are passed through a sponge oil section 15 to which lean sponge oil from a source 6 is fed by means of a line 5 which sponge oil extracts any contaminating gasoline-type hydrocarbons from the acid gas. The acid gas thus treated then passes to storage by means of a line 16. The rich sponge oil leaves the sponge oil section via a line 17, and may be regenerated for further use.

The process according to this invention is especially attractive due to the reduced amount of liquid absorbent required for the absorption of a given amount of acid gases as compared with the absorption of a similar amount of acid gas by means of an aqueous alkanolamine solution. One of the further important advantages of the use of the mixed absorbent of this invention compared with aqueous amine absorbents lies in the small heat capacity of the mixed amide-alkanol amine absorbent as compared with aqueous amine. For example, the heat capacity of a mixture of 20% diethanol amine and 80% dimethyl formamide is only about half of that of an aqueous diethanolamine solution. Moreover, the heat of desorption of hydrogen sulphide in the mixed solvent is somewhat lower, and hydrogen sulphide stripping is easier at the temperatures employed in the process of this invention. Consequently, for a given volumetric flow of absorbent the process heat load is lower and the cooling water requirements are much lower.

The hydrogen sulphide extracted from a sour feed by the process according to the invention can be used for the preparation of elemental sulphur. This may be done by the well-known Claus sulphur process. An attractive alternative is the injection of sulphur dioxide into the absorber column. According to this modification of the process, the sour gas is fed into the absorber column for contact with the mixed absorbent and at the same time sulphur dioxide is injected into the column. This sulphur dioxide reacts with hydrogen sulphide absorbed in the mixed solvent from the sour gas feed, forming elemental sulphur in a form of a heavy, rapidly settling precipitate. This is in contrast to the very finely divided milky sulphur precipitate obtained in aqueous alkanolamine media. The unabsorbed sweet gases pass out of the absorption section where they may be, and preferably are scrubbed with a lean amide-alkanolamine solution for the removal of any excess sulphur dioxide which may have remained in the unabsorbed stream as it passes from the absorption section. Preferably, the scrubbed dry sweet gas then passes through a sponge oil section for the purpose of removing any gasoline-type hydrocarbons which may be present.

The absorption medium, now containing

suspended elemental sulphur, is conducted to a sulphur settler where sulphur settles to the bottom and the mixed absorbent, containing water of reaction, is heated sufficiently to evaporate the water after which the regenerated lean absorbent mixture is recycled to the absorber column for treatment of further quantities of sour gas. The volatilized water is removed from the settler. The sulphur dioxide added to the absorber column in this version of the process of the invention may come from an extraneous source or may be obtained by oxidation of part of the sulphur with oxygen by known means.

EXAMPLE II (see Figure II).

A natural gas containing about 14% hydrogen sulphide, the remainder being light hydrocarbons and inert gases, was treated according to the process of the invention. The sour gas feed from a source 101 is injected into the lower section of the rectified absorber column 102 fitted with a reboiler (not shown) and fractionation plates (not shown), under a pressure of about 70 kg/cm² and a temperature of about 35°C. The bottom of the absorber column is maintained at a temperature of about 75°C by means of a reboiler (not shown), while the top section of the absorber column has a temperature of about 35°C to 38°C. The lean mixed absorbent, comprising 6% by weight of water, 30% by weight of diethanolamine and 64% by weight of sulpholane, enters the absorber column 102 by means of a line 103 at a temperature of about 35°C. Hydrogen sulphide and a small amount of hydrocarbons (substantially smaller proportions of hydrocarbons than with anhydrous absorbent) are absorbed by the lean absorbent mixture from the sour feed. Sweet hydrocarbon gas leaves the absorption section of the absorber column by means of a line 104.

The fat absorbent, containing absorbed acid gases leaves the bottom of the absorber column 102 by means of a line 105 and passes under substantially reduced pressure through a heat exchanger 107 to a stripper column 108 which is heated by means of a reboiler 109. The fat absorbent enters the acid gas stripper column preferably at a pressure of about 1.7 kg/cm² abs. The bottom of the stripper has a temperature of about 150°C. Under these conditions, acid gases are stripped off and pass from the acid gas stripper by means of a line 109A, after having passed through a sponge oil section 110 at the top of the acid gas stripper column. The fat sponge oil, containing absorbed gasoline-type hydrocarbons is sent by means of a line 111 to a hydrocarbon stripper (flash) column 112 to strip off the absorbed hydrocarbons, which pass to storage from the top of the column 112 by means of a line 113. The lean sponge oil then returns to the sponge oil

section of the acid gas stripper column by means of a line 114.

5 The regenerated mixed absorbent leaves the bottom of the acid gas stripper by means of a line 115 to be sent back to the top of the acid gas absorber column by means of a line 103 via the heat exchanger 107 and a further heat exchanger 106.

10 In a preferred form of the process a bleed stream of the regenerated mixed absorbent is sent via a line 117 to an absorbent drying column 116. In this column extraneous impurities which naturally build up in the absorbent mixture during the foregoing treating procedures are removed, while in the course of this "clean up" water may also be removed, via a line 119, to produce an essentially dry (water-free) mixture of dialkanolamine and sulpholane. This dry mixed absorbent is then recycled from the bottom of the absorbent drying column 116 by means of a line 118 to the top of the acid gas absorber column 102. In the top section of the absorber column the dry absorbent serves to remove any remaining water from the sweet gas as it approaches the top outlet of the absorber column. Thus, the water content of the effluent sweet gas is reduced to permissible limits of about 0.1 kg per 1000 m³ of sweet gas. The dry absorbent then descends the column, mixing with the water-containing mixed absorbent and performing its original function of absorbing hydrogen sulphide.

35 The bleed stream utilized for this purpose will be about 1 to 4% based on the total wet mixed absorbent being utilized throughout the system. The proportion of the bleed stream is kept to a minimum so as to maintain an accurate proportion of water at the desired points, particularly in the acid gas absorber column and in the acid gas stripper column.

45 The mixed aqueous absorbent is preferably employed in amounts of 0.4-0.8 moles of aqueous mixed absorbent per mole of feed gas. The effluent from the absorber column contains only mere traces of hydrogen sulphide, normally about 1 to 5 ppm.

EXAMPLE III.

50 Figure III shows in more detail a preferred version of the process of this invention, wherein a water-containing mixed absorbent containing sulpholane is used. According to Figure III the acid-containing hydrocarbon feed gas from a source 201 enters the lower portion of a high pressure absorber column 202 and rises against a descending stream of the aqueous mixed absorbent, which enters through a recycle line 203 into the upper portion of the column 202. The fat absorbent leaves by means of a line 205 at the bottom of the high pressure absorber column and proceeds to a partial flasher 219 wherein the pressure is sharply

reduced and the temperature adjusted sufficiently to cause a rapid flashing of a major portion of the acid gases together with non-aromatic hydrocarbons, both light and/or heavy (i.e. gasoline-type) and both saturated and/or unsaturated. The acid gases and hydrocarbons then proceed to an oil scrubber 221, where lean sponge oil, entering the scrubber via a line 250, removes the hydrocarbons; the hydrocarbon-free acid gas leaves the scrubber at the top via a line 222. The fat sponge oil leaving the scrubber via a line 251 is regenerated in a normal way.

At least part of the partially flashed absorbent, having a substantially reduced acid gas content, is recycled by means of a line 223 from the bottom section of the partial flasher 219 and through a pump 224 to the mid section of the high pressure absorber column 202. The function of this recycle is to utilize the reserve dissolving power of the partially flashed absorbent to remove further quantities of acid gases from the feed in the absorber column. The remaining portion of the partially flashed fat absorbent proceeds by means of lines 223 and 225 to a fat absorbent stripper 208 below the cold upper section 206 thereof which is cooled for instance by a water cooling coil 253. The substantially pure acid gases leave the stripper 208 via lines 209A and 252 for further use, for instance in a Claus sulphur plant.

The stripped absorbent leaves the stripper 208 at the bottom by means of a line 215. A part of this stream is recycled by means of the line 203 to the upper part of the high pressure absorber column 202 to perform its function of absorbing acid gases. A small portion (1-4% of the stripped absorbent) is taken as a bleed stream 217 to an absorbent drying column 216. Here, under reduced pressure, water is removed at the top of the column together with any aromatic hydrocarbons and sent, after condensation and cooling in a cooler 254, to a phase separator 226. The aromatic hydrocarbon layer which separates from the water is removed by a line 227 to storage and water is discarded from the bottom layer by means of a line 228.

115 If the acid gas leaving the oil scrubber 221 still contains any residual normally gaseous hydrocarbons it may be recycled at least in part via the line 222 through a compressor 229 and a line 230 to the feed gas source 201.

120 In this way the recovery of the light hydrocarbons from the acid gas is improved by a second passage through the absorber column.

125 The advantage of having the oil scrubber 221 for saturated hydrocarbons located downstream from the partial flasher 219, is that the non-gaseous hydrocarbons are more conveniently removed than from an oil scrubbing section located downstream from the

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fat absorbent stripper 208. This is true because the pressure is higher and the total acid gas stream is smaller.

The phase separator 226 yields almost pure acid-gas-free aromatic hydrocarbons. This is made possible in the present process by the very high selectivity of the sulpholane portion of the mixed absorbent between aromatic and non-aromatic hydrocarbons in the sense that the volatility of the aromatics is depressed by a greater order of magnitude than the volatility of the corresponding non-aromatics of comparable boiling points.

The fractional recycle of partially flashed solvents from the flasher 219 to the mid-section of the high pressure absorber column 202 has the objectives of, first, minimizing the relative amounts of solvents which are exposed to the high temperature regions of the process, so reducing the heat load of the process and reducing thermal degradation of the organic components of the absorbent as well as reducing cooling water requirements. Secondly, it utilizes spare acid gas absorbing capacity of the physical solvent, in a region of the high pressure absorber column where the main purpose is to remove the bulk of the acid gas and not to reduce the acid gas level to very low values.

By these alternative forms of the process, it is therefore possible to partition normally liquid aromatic from non-aromatic hydrocarbons to obtain separate products. This is not possible when employing an aqueous alkanolamine as the acid gas absorbent.

The aqueous mixed absorbent of the invention also makes it possible to handle feed gases containing large amounts of normally liquid hydrocarbons, which is not possible with an ordinary aqueous alkanolamine absorbent. This is due to the fact that if such streams were so treated, any liquid hydrocarbons phase would separate out at the bottom of the high pressure absorber column due to the very limited hydrocarbon solubility in aqueous alkanolamines. The process is very flexible in that it is possible to achieve desired degree of rejection and/or partition of these normally liquid hydrocarbons.

WHAT WE CLAIM IS:—

1. A process for removing acidic gases from a gaseous mixture which comprises contacting a gaseous mixture with a liquid absorbent comprising a basic component consisting of at least one amine having a weakly basic character in the range of pK_b at 25°C of 3-14, and a selective solvent comprising at least one component selected from aliphatic carboxylic acid amides, cyclotetramethylene sulphone and its derivatives and perhalo alkanes, and separating the resulting essentially acid-free gas from the liquid absorbent containing the absorbed acidic gases.

2. A process as claimed in Claim 1 in

which the absorbent contains 1 to 15%wt. of water.

3. A process as claimed in Claim 1 or Claim 2 in which the amine content of the absorbent is from 7.5 to 70% wt.

4. A process as claimed in Claim 1 or Claim 2 in which the amine content of the absorbent is from 15 to 35% wt.

5. A process as claimed in Claim 1 or Claim 2 in which the amine content of the solvent is from 20 to 30% wt.

6. A process as claimed in any of Claims 1 to 5 in which the amine is an alkanolamine.

7. A process as claimed in Claim 6 in which the amine is a dialkanolamine.

8. A process as claimed in Claim 7 in which the amine is diethanolamine.

9. A process as claimed in Claim 7 in which the amine is diisopropanolamine.

10. A process as claimed in any of Claims 1 to 9 in which the sulphone is tetra-hydro-methylene sulphone.

11. A process as claimed in any of Claims 1 to 10 in which the gaseous mixture is contacted with the absorbent at a pressure in the range 7 to 70 kg/cm²abs.

12. A process as claimed in any of Claims 1 to 11 in which the gaseous mixture is contacted with the absorbent counter-currently in an absorber column equipped with contacting means.

13. A process as claimed in any of Claims 1 to 12 in which the contacting is effected at a temperature in the range 25 to 135°C.

14. A process as claimed in any of Claims 1 to 13 in which the absorbed gases are removed from the absorbent in a stripper at a temperature in the range 112°C to 190°C and a pressure in the range 1 to 3.5 kg/cm²abs.

15. A process as claimed in any of Claims 1 to 14 in which the contacting takes place in an absorber column and the bottom product of the absorber column is freed from the major part of the absorbed gases in a flashing zone, the bottom product of which flashing zone is lead into a stripper.

16. A process as claimed in Claim 15 in which the pressure in the flashing zone is in the range 1.15 to 8 kg/cm²abs.

17. A process as claimed in any of Claims 1 to 16 in which the absorbent also absorbs gasoline-type hydrocarbons from the gaseous mixture, the absorbed substances are stripped as gasses from the absorbent and the stripped gases are washed with a sponge oil for removal of the gasoline-type hydrocarbons.

18. A process as claimed in any of Claims 1 to 17 in which the absorbent is regenerated and in which a part of the regenerated absorbent is substantially dried and subsequently mixed with the balance of the regenerated absorbent.

19. A process as claimed in Claim 18 in which the drying is effected by stripping in

an absorbent drying column.

5 20. A process as claimed in Claim 18 or Claim 19 in which the contacting takes place in an absorber column and in which the dried absorbent is introduced near the top of the absorber, above the inlet of the main absorbent stream.

10 21. A process as claimed in any of Claims 1 to 20 in which the acidic gases contain hydrogen sulphide and are partially oxidized to sulphur.

15 22. A process as claimed in Claim 21 in which the contacting takes place in an absorber column and the hydrogen-sulphide-containing gas is oxidized to sulphur in the absorber column by injecting sulphur dioxide gas into the absorber column.

20 23. A process as claimed in Claim 22, in which the absorbent containing dispersed sulphur is freed from sulphur and subsequently

further processed for the removal of absorbed gases.

24. A process for the removal of acidic gases from gaseous mixtures substantially as described with reference to any of Examples I to III and the respective Figures I to III of the accompanying drawings.

25 25. Hydrocarbon gases freed from acidic gases by a process as claimed in any of the preceding claims.

30 26. Hydrogen sulphide obtained by a process as claimed in any of Claims 1 to 21.

27. Sulphur produced by a process as claimed in any of Claims 21 to 23.

35 28. Gasoline-type hydrocarbons produced by a process as claimed in Claim 17.

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Chartered Patent Agents.
Agents for the Applicants.

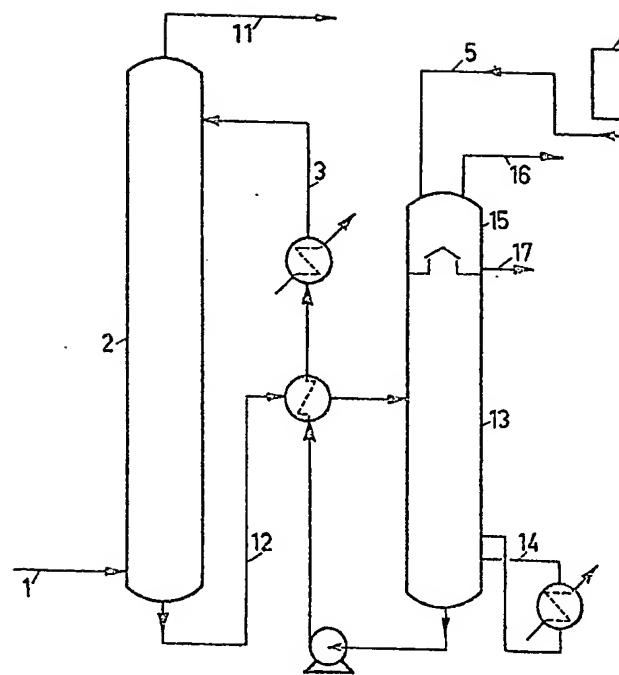


FIG. I

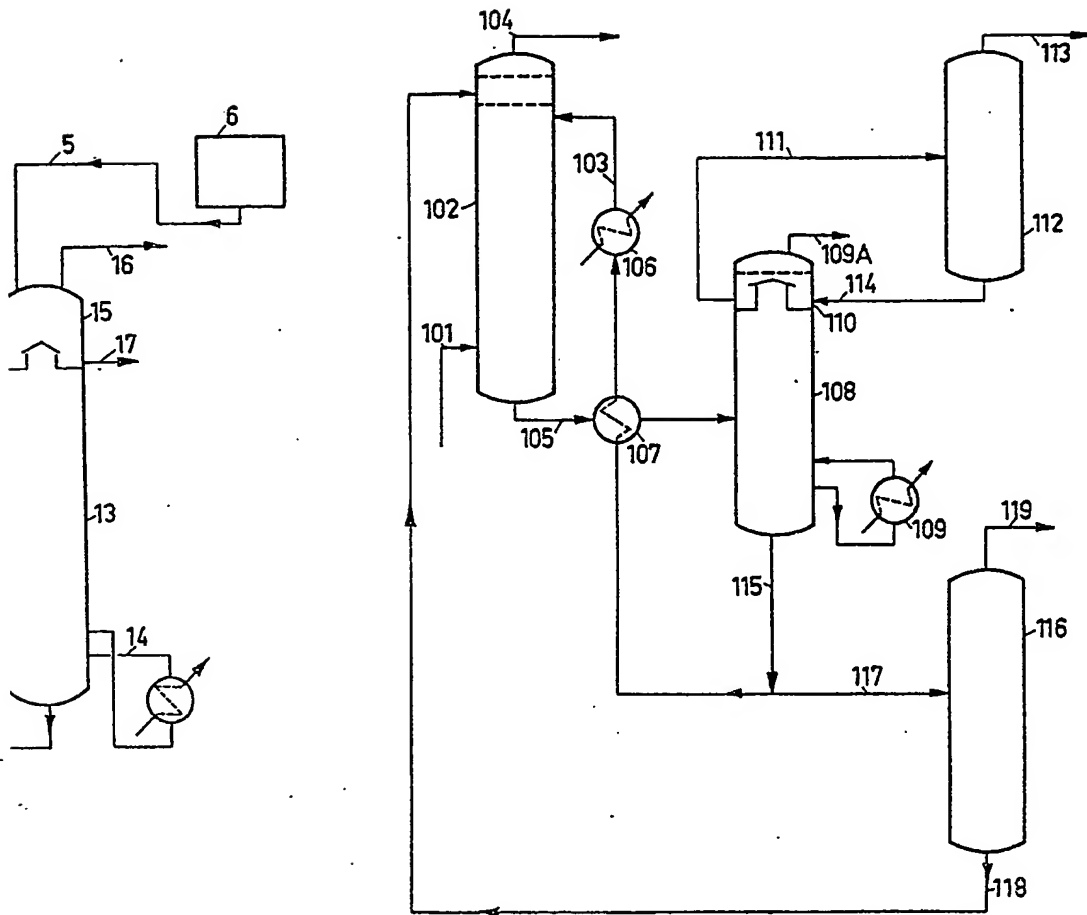


FIG. II

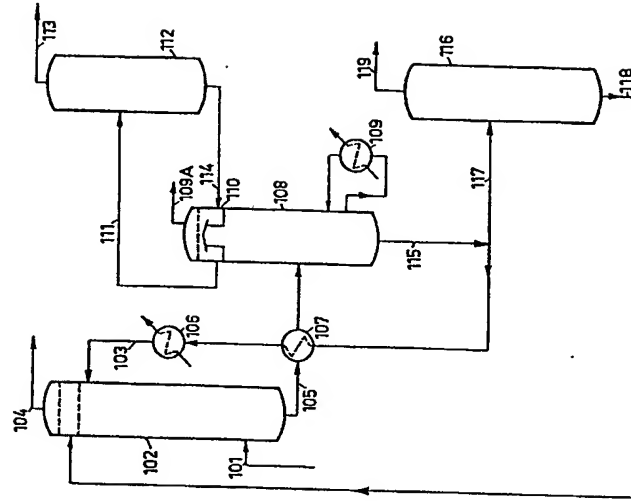


FIG. II

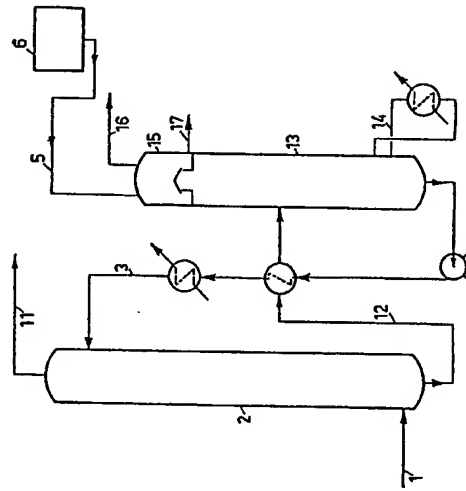


FIG. I

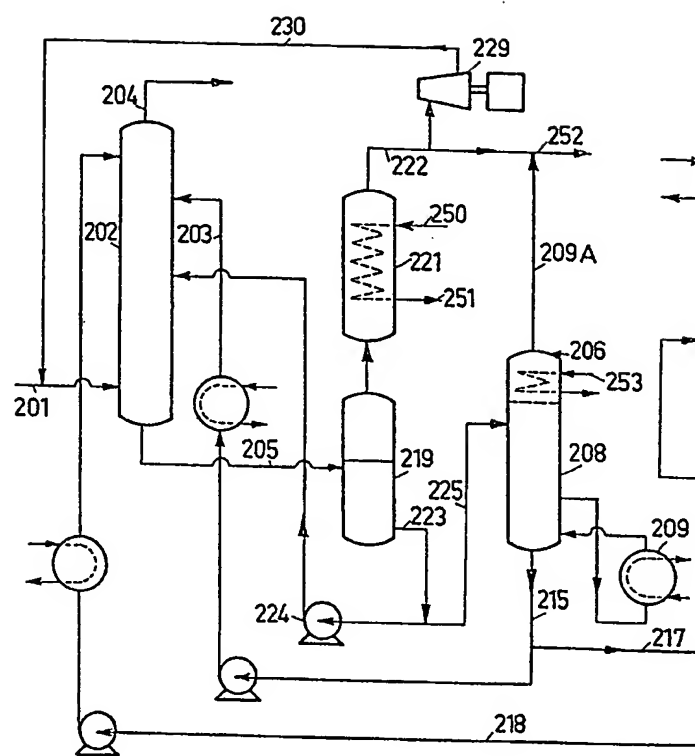


FIG. III

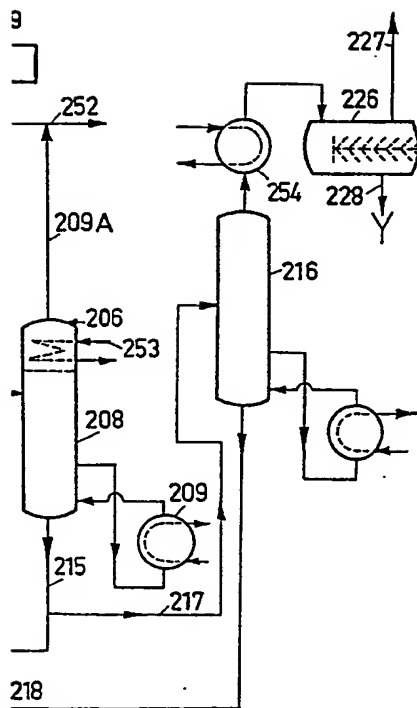


FIG. IV

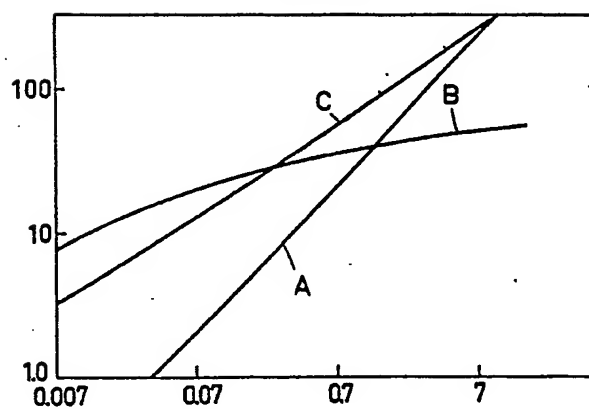


FIG. V

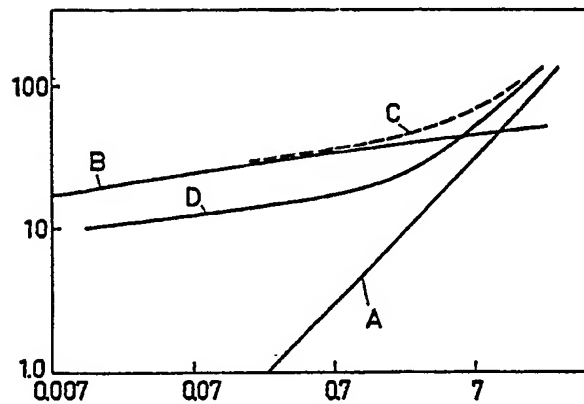


FIG. IV

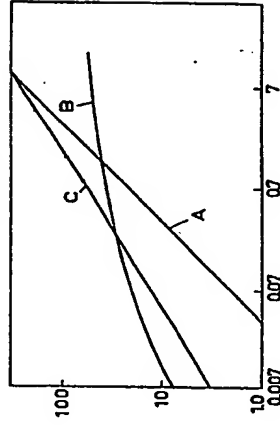


FIG. V

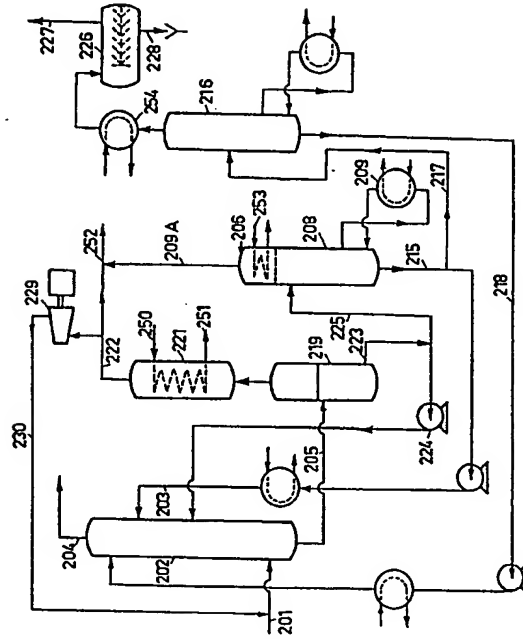
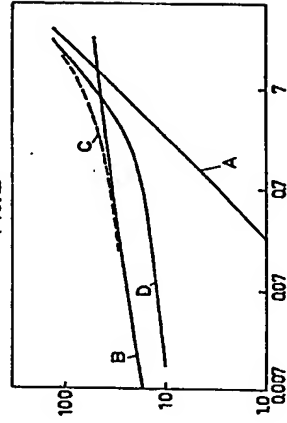


FIG. III

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